DIFFUSION IN TWO-PHASE SYSTEMS

BY

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AN ABSTRACT OF A THESIS

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DIFFUSION IN TWO-PHASE SYSTEMS

In chemical engineering operations which involve the transport of molecules between phases, the interface has always been assumed to offer no resistance to mass transfer. This assumption was made purely for the convenience in calculation and design. Recently investigations in physiological field, (1), (2), (3), indicated that there might be considerable resistance to diffusion at a liquid-liquid interface. It was the purpose of the present work to examine more carefully the diffusional process across a liquid-liquid interface.

Measurements were made on both binary and ternary liquid systems at temperatures close to the critical solution temperature. The binary system was the sulfur dioxide - normal heptane system and the ternary was the water-phenol-sulfuric acid system. Radioactive traces were used to eliminate the effect of concentration changes during the diffusion.

Two apparatuses were used in the present investigation. The one designed for the sulfur dioxide - n-heptane system was capable to withstand mild pressures to overcome the vapor pressure of sulfur dioxide. The main part of the apparatus consisted of a stainless steel piston which fitted in a stainless steel cylinder. The two diffusion cells were 3/8 inch holes drilled on the piston and the cylinder respectively. Thus by moving the piston from one position to another the cells could be lined up or separated. The cells were filled with diffusing liquids when they were separated and then they were lined up to start the diffusion. In the cells were closely packed stainless steel screens to prevent convection.

The second apparatus, designed for the non-volatile water-phenol-sulfuric acid system, consisted mainly of a stainless steel tube, at the bottom of which a thin stainless steel ring loosely packed with stainless steel screens were situated. This thin stainless steel ring served as the bottom cell. Another

stainless steel ring also loosely packed with stainless steel screens served as the top cell. This upper ring after soaked with the diffusing liquids was slided down the stainless steel tube to come into contact with the other ring filled also with the liquids.

Scintillation counter, as described by Timmerhaus (4), was used for analysis in both apparatuses. The scintillation crystal was placed at one end of the cell and the light pulses was conducted out by means of quartz and lucite rods. This arrangement enabled a continuous analysis of the concentrations at one end of the cell.

The differential equation for the diffusion in two-phase systems under the present boundary conditions was solved. In solving it, the flux function at the interface was assumed to be proportional to $(C_- - mC_+)$, where C_-, C_+ are the concentrations at the interface and m is the distribution coefficient. The transfer coefficient at the interface α was the proportional constant. The calculation of α from an experimental run required the knowledge of the diffusion coefficients in the corresponding two phases. Thus in the present experiments these coefficients were also measured.

The experimental results were shown in Tables I and II.

Table I. shows the results of the sulfur dioxide - n-heptane system, which has a critical solution temperature of 19°C (5). D_1 is the diffusion coefficient of $S^{35}O_2$ in n-heptane saturated liquid sulfur dioxide. D_2 is the diffusion coefficient of $S^{35}O_2$ in sulfur dioxide satuarted n-heptane. m is the distribution coefficient of $S^{35}O_2$ in sulfur dioxide and n-heptane layers. α is the interfacial transfer coefficient of $S^{35}O_2$ diffusing from the sulfur dioxide rich layer across the interface into the n-heptane layer.

TABLE I

Temperature °C	$D_1 \times 10^5$ cm²/sec	$D_2 \times 10^5$ cm²/sec	m	$a \times 10^5$ cm/sec
0.5	4.83	43.4	8.9	1.10
15.0	8.22	7.85	5.2	4.33

Table II. presents the results of the water-phenol-sulfuric acid system. This system was made by a mixture of 44% phenol and 56% 0.1 N sulfuric acid and has a critical solution temperature of 70.5°C (6). D_1 is the diffusion coefficient of $H_2S^{35}O_4$ in the water rich layer of the above mixture. D_2 is the diffusion coefficient of $H_2S^{35}O_4$ in the phenol rich layer. a is the interfacial transfer coefficient of $H_2S^{35}O_4$ diffusing from the water rich layer across the interface into the phenol rich layer.

TABLE II

Temperature °C	$D_1 \times 10^5$ cm²/sec	$D_2 \times 10^5$ cm²/sec	m	$a \times 10^5$ cm/sec
22.0	0.339	0.140	13.6	0.265
40.0	0.0719	0.448	14.8	0.0259

The followings can be concluded from the present investigation:

1. The existence of resistance to diffusion at a liquid-liquid interface was believed to be general and not negligible in treating transport problem between phases.

2. The constant a was found experimentally to be a true coefficient to represent the case of molecules diffusing through an interface between two liquid phases.

3. a for liquid $S^{35}O_2$ diffusing in the sulfur dioxide -n-heptane system was measured and found to increase as temperature increased from 0.5°C to 15°C.

4. a for $H_2S^{35}O_4$ diffusing in the water-phenol-sulfuric acid

system was measured and found to decrease as temperature increased from 22°C to 40°C. The system water-phenol-sulfuric acid was found abnormal in that (a) the distribution coefficient m increased, rather than to decrease as normally would be expected, as the temperature increased from 22°C to 40°C.; (b) the diffusion coefficient of $H_2S^{35}O_4$ in the water rich layer of the system decreased as temperature changed from 22°C to 40°C while the diffusion coefficient in the phenol layer increased.

5. Any relation between a and surface tension was not apparent.

BIBLIOGRAPHY

1. Irwin, M., Proc. Soc. Exptl. Biol. Med., 26, 125 (1928).

2. Danielli, J.F., Trans, Faraday Soc., 37, 121 (1941).

3. Sjölin, S., Acta Physio, Scand. 4, 365 (1942).

4. Timmerhaus, K.D., M.S. Thesis, University of Illinois (1949).

5. Leslie, R.T., J. Research Natl. Bur. Standards, 13, 589 (1934).

6. Dubrisay and Toquet, Bull. Soc. Chim. France, 25, 354 (1919).

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With Chang, T.L., "The Landolt Reaction in Heavy Water" J. Chinese Chem. Soc. **16**, 1 (1949).

with Chang, T.L., "The Density of Heavy Water between 25°C and 100°C" Chinese J. Phys. **7**, 230 (1949).

with Timmerhaus, K.D., Giller, E.B., Duffield, R.B. and Drickamer, H.G., "A High Pressure Fitting for Scintillation Counting" Rev. Sci. Instr. **21**, 261 (1950).

with Drickamer, H.G. and Mellow, E.W., " A Modification of the Theory of the Thermal Diffusion Column" J. Chem. Phys. **18**, 945 (1950).

with Drickamer, H.G., "Thermal Diffusion in the System Methane-xenon" J. Chem. Phys. **18**, 1031 (1950).

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